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(54) Ferritic iron-aluminium-chromium alloys.

(57) A ferritic alloy of iron, chromium and aluminium containing:

10 to 25% chromium
1 to 10% aluminium
0 to 0.15% carbon
0 to 3% silicon
0 to 2% manganese
0 to 2% titanium
0 to 5% nickel, the nickel content not however being so great as to produce significant amounts of a second phase,
hafnium, 0.05 to 1%
the balance being iron and incidental amounts of the other alloying elements.

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FERRITIC IRON-ALUMINIUM-CHROMIUM ALLOYS

The present invention relates to ferritic alloys of iron, chromium and aluminium containing a significant amount of hafnium.

Ferritic iron-chromium-aluminium alloys are known and are in use particularly in environment where resistance to oxidation is of importance. We have found that the oxidation resistance of these alloys and particularly their resistance to oxidation in the presence of sulphur and oxygen, as may be encountered in combustion atmospheres, can be greatly enhanced by small additions of hafnium.

Accordingly, the present invention provides a ferritic alloy of iron, chromium and aluminium containing:-

10 to 25% chromium
1 to 10% aluminium
0 to 0.15% carbon
0 to 3% silicon
0 to 2% manganese

0 to 5% nickel, the nickel content not however being so great as to produce significant amounts of a second phase,

0 to 2% titanium, and from 0.5 to 1% hafnium, the balance being iron and incidental amounts of other alloying elements.

Preferably the alloys contain 15.5 to 25% chromium and 4.5 to 10% aluminium.

Preferably the alloys contain from 15.5 to 18% chromium.

Preferably the alloys contain from 4.5 to 6% aluminium e.g. about 5%.

The percentage of nickel is chosen so that it is not so great within the range quoted above as to produce significant amounts of a second phase taking into account the amounts chosen for each of the other ingredients of the alloy. Preferably, the amount of nickel does not exceed 0.5%.

Other rare earth metals may be used in addition to hafnium, e.g. yttrium, zirconium in an amount up to 2% or more preferably in an amount up to 1% or the commercially available alloy known as mischmetall in an amount up to 1%. Naturally, the principal ingredients of mischmetall, cerium and lanthanum, may be used individually if desired.

The presence of incidental amounts of molybdenum, copper, tungsten and cobalt above the impurity level can be tolerated provided these elements are not present in excess. Other elements such as sulphur, phosphorus and

vanadium may be present as impurities but are not desirable.

The alloys may be manufactured by the processes normally used for making alloys of this general type. For instance, the alloys may be made by induction melting, either in air or using inert atmosphere or vacuum as appropriate, cast into ingots and subsequently forged or rolled into billet or slab prior to working down to strip, bar, wire or any other commercially saleable form.

In a typical small scale process for producing an iron-chromium-aluminium steel of the invention, a charge of high purity iron and low carbon ferrochromium is melted down in a basic lined induction furnace, either in air under a basic slag, or under an inert atmosphere or in vacuo, without slag, as is appropriate. When completely melted, the appropriate additions of aluminium, ferrotitanium and hafnium metal are added, in that order, the metal brought to temperature and cast into an appropriate ingot mould.

The invention will be illustrated by the following examples. Alloys according to the invention were prepared having the compositions shown below by the process described above.

The size of melt was 10 kg. giving a 2½" (60 mm) sq ingot. This was then heated to about 1100°C and forged under a 10 cwt hammer to produce suitable test bar. For the purpose of comparison, alloys not in accordance with the invention were prepared having the compositions shown below.

The resistance of these steels to oxidation was compared by the following scaling test procedure.

Specimens some ½" (13 mm) in diameter by 1¼" (30 mm) long were machined from bar and ground to a 120 grit finish. They were washed and cleaned in alcohol prior to test.

The test was of relatively short duration but involved cycling between ambient and test temperature. The test chamber was an alumina tube 2" (50 mm) internal diameter in which the sample was positioned across an open ended alumina boat. Heating was by means of the concentric electric furnace, the temperature being measured by reference to a noble metal thermo-couple, the hot junction of which was immediately above the specimen. The test atmosphere was produced by burning natural gas using excess air over that required for combustion, the flow rates being 1.4 cubic foot and 1.14 cubic foot (0.04 and 0.4 cubic metres) per hour respectively for gas and air. The combustion product, a mixture of nitrogen, oxygen, carbon dioxide and steam was pre-heated to test temperature before passing through the test chamber; test temperature was established prior to inserting the sample so that heating was rapid. Each test cycle was for six hours, after which the specimens were removed from the test chamber and cooled in a closed container so that any oxide scale which became detached was collected. When cold, the specimen was weighed, together with any detached scale and then scrubbed with a stiff bristle brush to remove any loosely adhering oxide

prior to re-weighing to get the starting weight for the next cycle. The whole procedure was repeated for a total of seven cycles and the total gain in weight, that is the sum of the individual gains, expressed as milligrams per square centimetre, for the 42 hour period, using the original surface area for the untested specimen, was taken as the scaling index.

The scaling indexes found for the steels tested are shown in the following Table.

TABLE

Example	COMPOSITION								SCALING INDEX (mgm/sq. cm.)		
	C	Si	Mn	Cr	Al	Ti	Hf	Cr + Al	1150°C	1200°C	1250°C
A	.005	.19	.07	14.08	4.60	.005	.53	18.68		0.99	322
B	.006	.38	.05	16.37	4.15	.44	.08	20.52	0.77		168
C	.005	.23	.03	15.86	4.05	.41	.18	19.91	61.9		400
D	.005	.17	.02	15.00	5.35	.50	.37	20.35	0.92		26.3
E	.005	.27	.06	15.94	4.83	.34	.46	20.77		0.56	0.89
F	.005	.17	.02	15.72	4.83	.0004	.63	20.55	0.65	2.21	4.23
G	.004	.16	.04	15.70	4.80	.42	.63	20.50	1.96	4.83	3.83
H	.005	.19	.03	17.75	4.67	.50	.39	22.42			1.92
I	.005	.19	.02	16.70	5.50	.49	.26	22.20			1.87
J	.010	.10	.06	16.54	5.21	.43	.11	21.75		0.88	0.97
K	.008	.09	.04	15.74	4.83	.38	.21	20.57		0.80	1.03
1	.041	.10	.08	15.84	5.36	.005	nil	21.20		4.07	445
2	-	-	-	12.6	4.3	nil	nil			403	

Samples A to C are in accordance with the invention but do not exemplify its most preferred embodiments. It can be seen that the scaling index of A at 1200°C is considerably improved over that of comparative Sample 1 and is still superior to that of comparative Sample 2 despite this latter containing much higher amounts of chromium and aluminium. The scaling index of Samples A to C is quite high however at 1250°C. Examples D to K which contain above 4.5% Al and 15.0% Cr show the still more superior characteristics of steels in accordance with the preferred practice of the invention and it can be seen that low scaling indexes are found even at 1250°C.

It can also be seen that the addition of titanium appears to confer a much smaller but still significant benefit in increased oxidation resistance to the steel containing hafnium. More significantly, the addition of titanium has a substantial effect in reducung the as-cast grain size of the steel and hence greatly improves its hot-working properties. In particular, it was observed that the cast structure of titanium-containing alloys such as B differed from that of alloys A and 2. It was noted that the addition of titanium appeared to have a marked effect on the crystallisation pattern, modifying the coarse columnar crystals of the normal product and giving a more uniform crystal distribution across the section.

Ingots of the steels were hot worked and it was noted that alloys containing titanium possessed added ductility

and less proneness to surface rupture. Resistance to cracking under thermal stress was enhanced.

Suitable fields of application for steels according to the invention are those in which resistance to oxidation at high temperatures is required. Examples of such uses are in the provision of electric furnace winding material or resistance heating wire generally and in the provision of knitted wire catalyst supports e.g. for use in vehicle exhaust systems for reducing emissions. Another field in which such properties are of value is in the construction of furnaces, for instance fluid bed combustion furnaces.

CLAIMS

1. A ferritic alloy of iron, chromium and aluminium containing:-

10 to 25% chromium

1 to 10% aluminium

0 to 0.15% carbon

0 to 3% silicon

0 to 2% manganese

0 to 2% titanium

0 to 5% nickel, the nickel content not however being so great as to produce significant amounts of a second phase,

characterised by containing from 0.05 to 1% hafnium the balance being iron and incidental amounts of other alloying elements.

2. An alloy as claimed in claim 1 containing from 15.5 to 25% chromium, from 4.5 to 10% aluminium.

3. An alloy as claimed in claim 1 containing from 15 to 18% chromium.

4. An alloy as claimed in any preceding claim containing from 4.5% to 6% aluminium.

5. An alloy as claimed in any preceding claim containing about 5% aluminium.

6. An alloy as claimed in any preceding claim containing not more than 0.5% nickel.

7. An alloy as claimed in claim 6 containing from 0.2 to 0.5% nickel.

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EUROPEAN SEARCH REPORT

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EP 81 30 0793

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	GB - A - 1 554 293 (YAZAKI SOGYO K.K.) * Claims 1, 6 and 8 * ---	1-7
A	GB - A - 1 542 694 (UNITED TECHNOL. CORPORATION)	
A	DE - A - 1 558 670 (US ATOMIC ENERGY COMMISSION)	
A	US - A - 3 591 365 (R. OHMACHI)	
A	FR - A - 2 165 453 (DEUTSCHE EDELSTAHLWERKE)	
A	DE - B - 1 558 657 (STAHLWERKE SÜDWESTFALEN) ---------	

CLASSIFICATION OF THE APPLICATION (Int. Cl.3)

C 22 C 38/18

TECHNICAL FIELDS SEARCHED (Int. Cl.3)

C 22 C 38/18
38/28
38/50
38/60

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	27.05.1981	RIES